



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D21H 23/76 // 17:29, 17:45, 17:55, 17:56, 17:68, 21:28, 21:30</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/23815</b> <b>(43) International Publication Date:</b> 4 June 1998 (04.06.98)
<b>(21) International Application Number:</b> PCT/GB97/03269 <b>(22) International Filing Date:</b> 27 November 1997 (27.11.97) <b>(30) Priority Data:</b> 9624832.3 28 November 1996 (28.11.96) GB <b>(71) Applicants (for all designated States except US):</b> ALLIED COLLOIDS LIMITED [GB/GB]; Low Moor, P.O. Box 38, Bradford, West Yorkshire BD12 0JZ (GB). AB CDM [SE/SE]; P.O. Box 37, Västra Frolunda, S-421 21 Göteborg (SE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ERIKSSON, Per-Ola [SE/SE]; Rapsvägen 11, S-892 33 Domsjö (SE). ERIKSSON, Ingvar [SE/SE]; Flygsjö 2173, S-890 37 Gideå (SE). HJALMARSON, Bo [SE/SE]; Framstvägen 7, S-804 25 Gävle (SE). LANGLEY, John, Graham [GB/GB]; Manderley, 101 Thorpe Lane, Guiseley, Leeds LS20 8NS (GB). <b>(74) Agent:</b> GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PRODUCTION OF PAPER AND PAPER BOARD  <b>(57) Abstract</b> <p>Paper or paper board is made by adding cationic polymeric retention aid to a cellulosic suspension, shearing the suspension to degrade the resultant flocs, aggregating the suspension by adding an aqueous composition of bentonite or other anionic bridging coagulant in the present of anionic dye, pigment or optical brightening agent, and forming paper from the aggregated suspension.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Production of Paper and Paper Board

This invention relates to the production of paper or paper board by a process comprising forming an aqueous cellulosic suspension, adding a polymeric retention aid to the suspension to form flocs, degrading the flocs by shearing the suspension to form microflocs, aggregating the microflocs by adding to the suspension an aqueous composition of an anionic bridging coagulant, draining the aggregated suspension to form a sheet, and drying the sheet. Processes of this general type are well known. For instance the Hydrocol (trade mark) process involves these process steps and utilises bentonite (i.e. an anionic swelling clay) as the anionic bridging coagulant. Such processes are described in, for instance, US 4753710, 4913775 and EP-A-707673.

The formation of the flocculated suspension generally involves the addition of one or more cationic polymers to the suspension. For instance the polymeric retention aid is often a high molecular weight cationic polymer, and/or other cationic polymers may be added at earlier stages in the process. For instance cationic starch or other strength additive can be added to increase strength and/or low molecular weight cationic polymers can be added to improve retention and/or for other purposes, such as controlling pitch in the thick stock.

In order to improve the visual appearance of the dried sheets, it is conventional to add an anionic material which will alter the visual appearance of the sheet, such as a pigment or dye or, usually, an optical brightening agent. For reasons of convenience and thorough mixing, these anionic materials are always added at a relatively early stage in the process, certainly before the retention aid and often even at the thick stock stage, for instance in the mixing chest.

Thus a typical process comprises adding an anionic optical brightener to the thick stock with or prior to any filler that is required and then adding cationic starch

and/or low molecular weight cationic coagulant (which may have also been added to the thick stock as a pitch control additive), then adding the cationic or other polymeric retention aid and then the anionic bridging coagulant.

5           Processes of this type have been operated on a very large scale for many years.

          In all paper making processes it is desirable to obtain optimum performance utilising a minimum amount of chemical additives. Thus the mill operator wants to  
10   achieve optimum pitch control, strength, retention and drainage or other dewatering using a minimum amount of polymer, and optimum visual appearance using a minimum amount of optical brightener, dye or pigment.

          The object of the invention is to provide improved  
15   performance in such processes. In particular, one object is to provide improved retention and dewatering (including drainage) performance so as to enable the operator either to use the same amount of chemical additives and obtain increased dewatering and retention performance or to allow  
20   the operator to achieve equivalent dewatering and retention performance but with a reduced amount of additives. Another object is to achieve improved visual appearance, thus allowing the operator to achieve increased brightening or colouring using the same dosage of optical brightener,  
25   dye or pigment, or to obtain equivalent brightening or colouring at a reduced dose of optical brightener, dye or pigment.

          According to the invention, a process for making paper or paper board comprises  
30   forming an aqueous cellulosic suspension,  
      adding a polymeric retention aid to the suspension to form flocs,  
      degrading the flocs by shearing the suspension to form microflocs,  
35   aggregating the microflocs by adding to the suspension an aqueous composition that includes an anionic bridging coagulant,

draining the aggregated suspension to form a sheet,  
and

drying the sheet,

and in this processes at least one cationic polymer is  
5 included in the suspension before the shearing and anionic  
optical brightening agent and/or dye and/or pigment for the  
paper or paper board is added to the suspension  
substantially with the anionic composition of anionic  
bridging coagulant.

10 Thus the anionic optical brightener, dye or pigment is  
added to the sheared suspension either just before, after  
or more usually with the aqueous composition of anionic  
bridging coagulant. The materials may be added to the  
suspension separately but at closely adjacent points or,  
15 more usually, they are added at a single addition point.  
Preferably therefore the anionic optical brightener, dye or  
pigment is mixed into the aqueous composition of anionic  
bridging coagulant prior to its addition over the  
suspension. Thus it may be mixed in-line as the aqueous  
20 composition is being fed towards the suspension or it may  
be pre-mixed.

The invention is applicable to any process where  
cationic polymer is included in the suspension before the  
shearing stage and anionic bridging coagulant is added  
25 subsequently. In practice this means that it is applicable  
to substantially all processes that involve the addition of  
polymeric retention aid followed by anionic bridging  
coagulant. This is because nearly all such processes do  
involve the addition of at least one cationic polymer at  
30 some stage prior to the shearing.

As a result of the invention we are able to obtain an  
improved combination of dewatering and retention properties  
and appearance properties.

The invention is of particular value when cationic  
35 polymer is included in the suspension before the shearing  
for the purpose of providing dewatering and retention,  
since the invention then provides improvement in dewatering

and retention properties. In preferred processes of the invention cationic polymer is included as a retention aid. It can be cationic starch for use as a retention aid as proposed in, for instance, US 4388150, but is preferably a  
5 cationic synthetic polymer having a molecular weight sufficiently high that it gives retention properties. Generally therefore its molecular weight must be above 500,000 and usually it has intrinsic viscosity of at least 4 dl/g. Intrinsic viscosity is measured by a suspended  
10 level of viscometer on an aqueous composition at 25°C buffered to pH 7.5.

The preferred cationic retention polymers are substantially water soluble copolymers of one or more ethylenically unsaturated monomers. Generally they are  
15 copolymers of acrylamide or other water soluble ethylenically unsaturated monomer with a cationic allyl monomer such as dialkyldimethylammoniumchloride (DADMAC) or a cationic acrylic monomer such as dialkylaminoalkyl(meth)-acrylates or acrylamides, either as acid addition or  
20 preferably quaternary ammonium salts. The polymers can be wholly linear or slightly crosslinked as described in EP 202780. The polymers can be amphoteric, as the result of the inclusion of a small amount of anionic groups. Suitable high molecular weight cationic polymeric retention  
25 aids which can be used in the invention are described in, for instance, US 4753710, 4913775 and EP-A-308752.

In processes of the invention of this general type using a high molecular weight cationic polymeric retention aid, it is often advantageous to pre-treat the suspension  
30 with other cationic polymer. This can be cationic starch (prior to a synthetic cationic polymeric retention aid) or other cationic strengthening resin or it can be a relatively low molecular weight highly charged cationic polymer that may modify the retention and dewatering  
35 properties. Suitable polymers of this type include polyethyleneimines, polyamines, polyDADMACS and dicyandiamide condensate polymers.

The invention also includes processes in which the cellulosic suspension is rendered cationic by the application of such polymers or is otherwise treated with such polymers, and a nonionic or anionic retention aid is then used. Such processes conducted using an anionic retention aid are described in EP-A-308752 and processes using non-ionic or anionic retention aids are described in EP-A-707673.

The invention is also of value when a cationic polymer, generally a highly charged low molecular weight cationic polymer such as any of those discussed above, is added at the thick stock stage, for instance to control pitch. Suitable low molecular weight cationic polymers are described in more detail in, for instance, EP-A-308752 and US 4913775.

The dosages of the cationic polymers used in the invention can be within conventional ranges. Thus the dosage of high molecular weight retention aid is generally from 50 to 2000, often 100 to 1000, g/t and the dosage of any low molecular weight cationic polymer is generally in the range 100 to 3000, often 500 to 2000, g/t. The optimum amount of any polymer in any process is determined by routine experimentation in conventional manner.

Although the total amounts used in the invention is generally within conventional ranges, the actual amount required to give any particular retention or dewatering performance in any particular process will generally be less than in a conventional process where the optical brightener, dye or pigment is added at an early stage. Typically the amount of cationic retention aid can, in the invention, be at least 5% and often at least 10% less than the amount that is required when the optical brightener, dye or pigment is added at an earlier stage. In some instances it can be up to 20 to even 30% less. For instance typically the amount is 10 to 100, often around 20 to 50 g/t less than in conventional processes.

The retention aid and any other previous polymer is added in conventional manner at a conventional position. It leads to flocculation and it is necessary in the invention, as is conventional, to degrade the flocs by shearing the suspension. Adequate shear may be achieved merely by flowing the suspension turbulently through a duct, in which event the retention aid can be added after for instance, the final centriscreeen. Generally, however, the degradation is achieved by passing the suspension through a relatively high shear mixing stage such as a centriscreeen or a fan pump.

Anionic bridging coagulant is then added (usually after the last point of high shear, eg at or approaching the head box) to the sheared suspension so as to aggregate the microflocs. This general technique is often referred to as supercoagulation or as microparticulate retention since most of the suitable anionic bridging coagulants are microparticulate materials.

The preferred material is bentonite, that is to say a swelling clay which is usually based on a smectite, hectorite or montmorillonite clay structure. However it is also possible to use other inorganic anionic microparticulate or colloidal materials such as colloidal silica, polysilicate microgel, polysilicic acid microgel and aluminum modified versions of these (see for instance US 4643801, EP-A-359552 and EP-A-348366). Anionic organic microparticulate materials can also be used. Thus anionic organic polymeric emulsions can be used. The emulsified polymer particles may be insoluble due to being formed of a copolymer of water soluble anionic monomer and one or more insoluble monomers such as ethyl acrylate, but preferably the polymeric emulsion is a crosslinked microemulsion of water soluble monomer material.

The particle size of the microparticulate material is generally below  $2\mu\text{m}$ , preferably below  $1\mu\text{m}$  and sometimes below  $0.1\mu\text{m}$ . For instance anionic crosslinked polymer emulsions having a size of  $0.01$  to  $0.2\mu\text{m}$  can be used.



Preferably however, the bridging coagulant is bentonite.

The amount of bridging coagulant is usually at least 300 g/t and often at least 1000 g/t, for instance up to 3000 or even 5000 g/t.

5       The anionic dye, pigment or optical brightener can be added to the suspension in whatever amount is conventional for that particular material for the effect that is desired. For instance commercial optical brightener compositions (such as the material sold under the trade  
10   name Blanchophor PO1) is typically used in amounts of 500 to 5000, often 1000 to 3000, g/t. The invention does allow a reduction in the amount of dye, pigment or optical brightener while maintaining equivalent visual effect, for instance, with reductions of 5 to 30% being typical.  
15   However it is usually preferred to use whatever amount of optical brightener, dye or pigment at the final stage that gives the desired visual appearance irrespective of how much might have been appropriate if it had been added at an earlier stage.

20       The cellulosic suspension may be made from any conventional fed stocks and may be clean or dirty. It may be filled or unfilled. If it is filled, the amount of filler in the suspension is typically 10 to 50% by weight of the total solid in the suspension. Conventional fillers  
25   may be used.

The following is an example.

A process was conducted in accordance with the general teaching of US 4913775. Thus filler was mixed into the suspension followed by 3.5 kg/t cationic starch followed by  
30   500 g/t polyDADMAC (IV about 1 dl/g) followed by 200 g/t high molecular weight cationic polymer followed by shearing in the centriscreeen followed by 1.5 kg/t bentonite. The cationic polymer was a copolymer of acrylamide and dimethylaminoethylacrylate quaternary salt having IV around  
35   7 to 10 dl/g.

In a first process, optical brightener was added before the filler in an amount of from 1 to 3 kg/t.

In a second process substantially the same amount of optical brightener was added after the starch but before the polyDADMAC.

5 In a third process substantially the same amount of optical brightener was added with the bentonite, as an aqueous composition containing both bentonite and the optical brightener.

10 It was found that the amount of cationic retention aid in the third process could be reduced by about 30 g/t (i.e. to 170 g/t) compared to the amount used in the first and second processes without any loss of dewatering and retention performance. Thus the third process, according to the invention, gave a 15% saving in cationic retention aid without any loss in dewatering or retention performance  
15 and while maintaining visual appearance.

CLAIMS

1. A process for making paper or paper board comprising  
forming an aqueous cellulosic suspension,  
5 adding a polymeric retention aid to the suspension to form flocs,  
degrading the flocs by shearing the suspension to form microflocs,  
aggregating the microflocs by adding to the suspension  
10 an aqueous composition of anionic bridging coagulant,  
draining the aggregated suspension to form a sheet,  
and  
drying the sheet,  
wherein a cationic polymer is included in the  
15 suspension before the shearing and an anionic dye, pigment or optical brightening agent for the paper or paper board is added to the suspension substantially with the aqueous composition of anionic bridging coagulant.
2. A process according to claim 1 in which the polymeric retention aid is selected from cationic starch and  
20 synthetic water soluble cationic polymer retention aids having intrinsic viscosity at least 4 dl/g.
3. A process according to claim 1 in which the polymeric retention aid comprises a water soluble cationic synthetic  
25 polymer formed from one or more ethylenically unsaturated monomers and having intrinsic viscosity of at least 4 dlk/g.
4. A process according to any preceding claim in which a cationic polymer is added to the suspension before the  
30 polymeric retention aid.
5. A process according to claim 4 in which the cationic polymer which is added before the retention aid is selected from polyDADMAC, polyimine, polyamine and dicyandiamide polymers.
- 35 6. A process according to any preceding claim in which the anionic optical brightening agent, dye or pigment is

included in the aqueous composition of anionic bridging coagulant before the addition of that to the suspension.

7. A process according to any preceding claim in which the anionic bridging coagulant is selected from organic and inorganic microparticulate materials.

8. A process according to any preceding claim in which the anionic bridging coagulant comprises bentonite.

9. A process according to any preceding claim in which anionic optical brightener is included with the anionic bridging coagulant.

# INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/GB 97/03269

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21H23/76 //D21H17:29,17:45,17:55,17:56,17:68,21:28,21:30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 753 710 A (LANGLEY JOHN ET AL) 28 June 1988 cited in the application see column 8, line 15 - line 34; claims ---	1-9
A	US 4 913 775 A (LANGLEY JOHN ET AL) 3 April 1990 cited in the application see column 8, line 32 - line 45; claims ---	1-9
A	US 4 969 976 A (REED ROBERT) 13 November 1990 see the whole document -----	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

6 March 1998

Date of mailing of the international search report

27. 03. 98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Koegler-Hoffmann, S

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/03269

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4753710 A	28-06-88	AU 578857 B	03-11-88
		AU 6811887 A	06-08-87
		CA 1259153 A	12-09-89
		EP 0235893 A	09-09-87
		FI 83349 C	22-08-96
		JP 1898108 C	23-01-95
		JP 6015755 B	02-03-94
		JP 62191598 A	21-08-87
		KR 9507186 B	03-07-95
		US 4913775 A	03-04-90
US 4913775 A	03-04-90	AU 578857 B	03-11-88
		AU 6811887 A	06-08-87
		CA 1259153 A	12-09-89
		EP 0235893 A	09-09-87
		FI 83349 C	22-08-96
		JP 1898108 C	23-01-95
		JP 6015755 B	02-03-94
		JP 62191598 A	21-08-87
		KR 9507186 B	03-07-95
		US 4753710 A	28-06-88
		AU 3174989 A	28-09-89
		CA 1322435 A	28-09-93
		DE 68905208 T	07-10-93
		EP 0335575 A	04-10-89
		ES 2053980 T	01-08-94
		FI 97307 B	15-08-96
		JP 2006683 A	10-01-90
		JP 5029719 B	06-05-93
		JP 5239800 A	17-09-93
		KR 9602733 B	26-02-96
		NO 174724 B	14-03-94
US 4969976 A	13-11-90	AU 3174689 A	28-09-89
		CA 1322436 A	28-09-93
		EP 0335576 A	04-10-89
		FI 92724 B	15-09-94
		JP 2006684 A	10-01-90
		NO 174723 B	14-03-94